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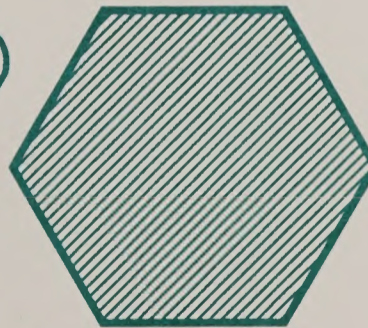
Technical Note 401

On-Site Mitigation of a High-Chromium Waste at the Exell Helium Plant

**By T.A. Davidson, D.E. Cornelius,
C.C. Fuller, and F.B. White
May 1998**

U.S. Department of the Interior

Bureau of Land Management



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On the Allegation of a High-Technology
State at the North Atlantic

by J. A. ... D. E. ... C. C. ...

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Abbreviations and Acronyms Used in this Report

AA	Atomic Absorption
CFR	Code of Federal Regulations
CO ₂	carbon dioxide
Cr-III	chromium in trivalent state
Cr-VI	chromium in hexavalent state
DEG	diethylene glycol
EPA	Environmental Protection Agency
FTIR	Fourier Transform Infrared Spectroscopy
H ₂ O	water
MEA	monoethanolamine
mg/L	milligrams per liter
ppm	parts per million
psig	pounds per square inch gauge
RCRA	Resources Conservation and Recovery Act
TAC	Texas Annotated Code
TCLP	Toxic Characteristic Leaching Procedure
TNRCC	Texas Natural Resources Conservation Commission

Symbols Used in this Report

°F	degrees Fahrenheit
"	inches
%	percent
\$	U.S. dollars

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Abstract

The Bureau of Land Management - Helium Operations has developed a cost-effective procedure to convert a water-soluble industrial waste bearing significant concentrations of toxic metals into a material that is environmentally compliant with the Resources Conservation and Recovery Act. A mixture of fly ash and Thio-Red was used to mitigate a chromium-bearing amine/glycol solution, a waste by-product of the gas treatment system at the Exell Helium Plant. The procedure was tested and proven to render the metals non-toxic according to performance-based treatment standards in 40 CFR 270.1(2)(vii) and 30 TAC 335.41(d)(3). Toxic Characteristic Leaching Procedure tests on composite samples were used to verify the environmental compliance.

¹ U.S. Department of the Interior, Bureau of Land Management - Helium Operations, Amarillo, Texas 79101-3545

Introduction

The mission of the Bureau of Land Management is to sustain the health, diversity, and productivity of public lands for the use and enjoyment of present and future generations. In support of this mission, the Bureau has developed a method for mitigating the toxic potential of a hazardous industrial waste to comply with the Resources Conservation and Recovery Act (RCRA).

The Bureau of Land Management - Helium Operations operates the Exell Helium Plant near Amarillo, Texas to produce and conserve helium. The first step in the helium production process is to scrub the feed gas stream with an amine/glycol solution in a contactor column (Figure 1) to remove acid gas components, such as carbon dioxide and water. This alkaline solution contains approximately 25% monoethanolamine (MEA), 70% diethylene glycol (DEG), and 5% chlorinated water. The MEA absorbs the acid gases, and the DEG absorbs water. The solution is then regenerated by being heated in a stripper column.

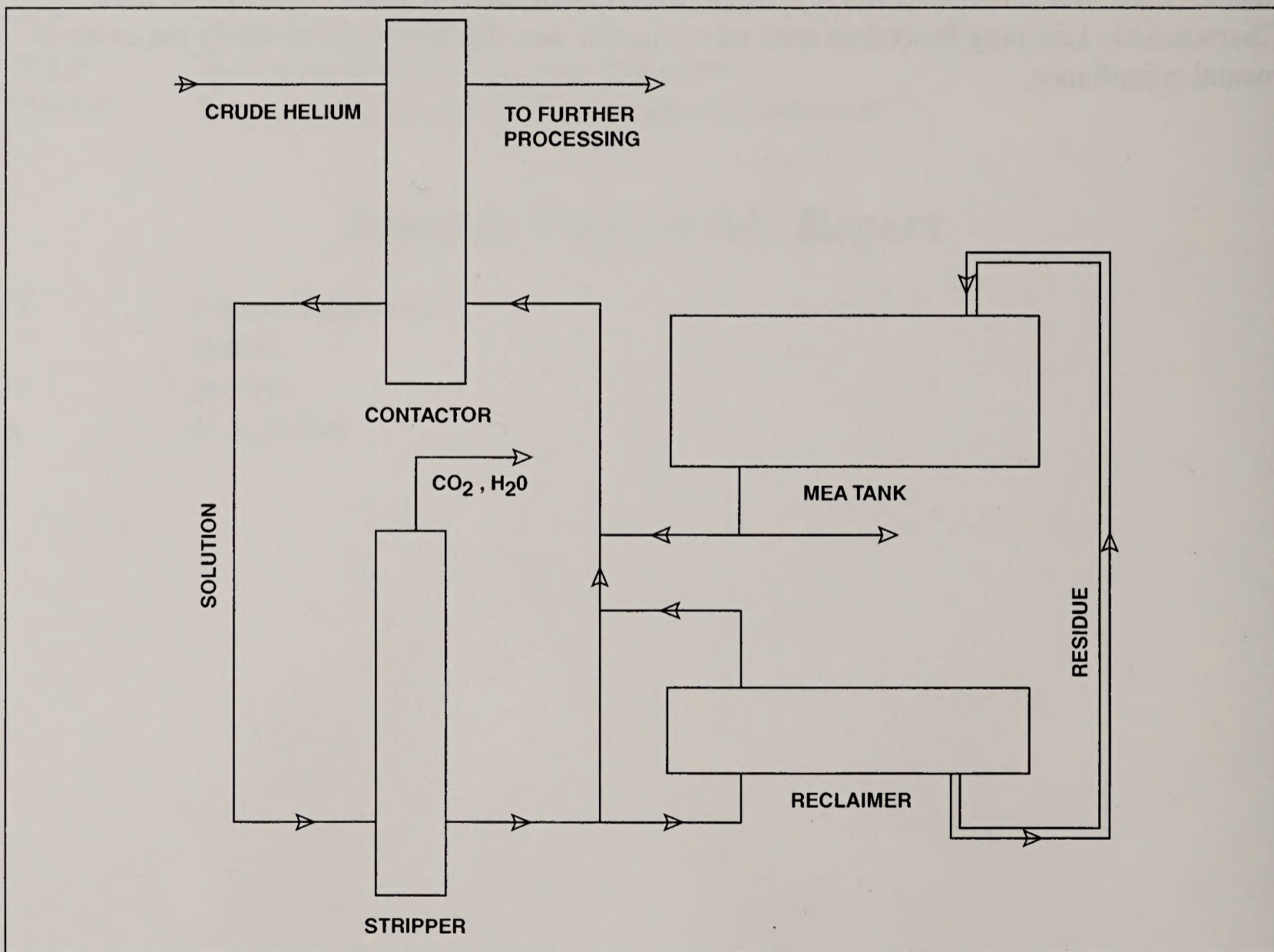


Figure 1: Diagram of the alkaline solution system with modifications for mitigation of the reclaimer waste.

The heated amine/glycol solution has proven corrosive to stainless steel components in the system. The corrosion was the result of the combination of high temperatures, high alkalinity, and high chloride levels from the chlorinated water makeup. The corrosion of this stainless steel introduced chromium and iron into the solution and resulted in the chemical degradation of the solution components, especially the MEA. Chromium is toxic and has been assigned the EPA Hazardous Waste Number D007 and a regulatory level of 5 mg/L.

The problem was aggravated by the decommissioning of the solution reclaimer (Figure 2) and removal of asbestos-bearing insulation, leaving the reclaimer inoperable. The solution reclaimer still was repaired and operated to remove impurities from a side stream of the solution. This was done by distilling the contaminated solution under a vacuum to separate the solution from the contaminants. The MEA and DEG were recondensed in a cooler and reintroduced to the solution system. The chromium-contaminated waste accumulated inside the kettle. The reclaimer still was shut down after chromium levels in the circulating solution dropped below 0.3 ppm.

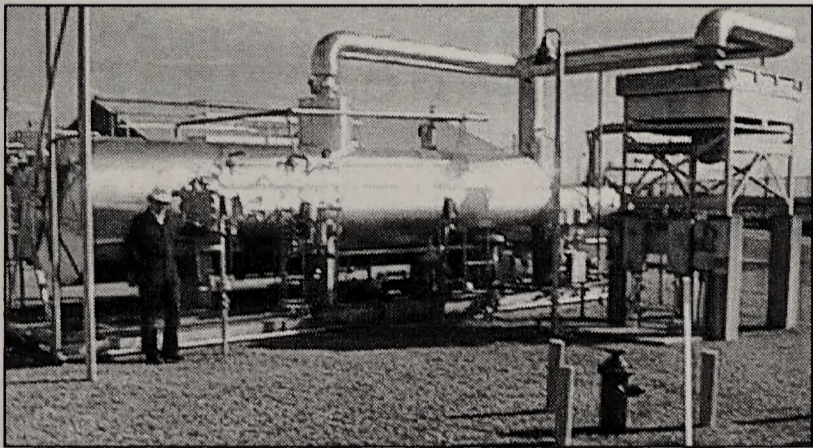


Figure 2: Solution reclaimer

The residue remaining in the bottom of the reclaimer tank consisted of chromium, iron oxides, and MEA degradation products, suspended in a base of DEG. This residue was determined by Atomic Absorption (AA) spectroscopy to average 250 mg/L of chromium (1).²

The Helium Privatization Act of 1996 (Public Law 104-273) mandated the closure and remediation of several Bureau facilities, including the Exell Helium Plant. To comply with this law, it became necessary to find a way to safely dispose of the accumulated residue.

The Helium Privatization Act of 1996 (Public Law 104-273) mandated the closure and remediation of several Bureau facilities,

Disposal of the reclaimer residue as hazardous waste under contract would have been very expensive. Estimates provided by industrial contacts suggested that the cost per 55-gallon barrel could be as much as \$10,000 to \$20,000, with consultation fees and required permits costing upwards of \$100,000, for a total estimated cost of almost \$300,000. A method was needed to economically convert the waste to a nonhazardous form for disposal.

² Italicized numbers in parentheses refer to items in the list of "References" at the end of this report.

Experimental

Analysis of the residue by Fourier Transform Infrared Spectroscopy (FTIR) showed the principal degradation product of MEA present was 2-hydroxyacetamide. Amides are moderately effective reducing agents. This suggested that the chromium present was entirely in the reduced or trivalent (Cr-III) state and that it was unlikely that any chromium would be present in the carcinogenic or hexavalent (Cr-VI) state. The means to confirm this suspicion, however, was not available; the AA spectrometer method used to certify the chromium content of the reclaimer waste is inherently insensitive to the difference between the two forms of chromium.

Small samples of the reclaimer bottoms were collected for experiments to develop a suitable disposal method. These experiments involved finding ways to optimize proportions of the waste with fly ash to achieve a stable matrix. Using a conservative assumption that all the chromium present in the reclaimer residue was in the carcinogenic Cr-VI form, a treatment regimen had to also include a reduction of any Cr-VI to Cr-III.

A commercially available product, Thio-Red (2), when added to the reclaimer bottoms and mixed with fly ash, proved to successfully reduce all of the chromium to Cr-III and bind the chromium in a stable fly ash matrix, as determined by Toxic Characteristic Leaching Procedure (TCLP) testing performed through a commercial laboratory (3). These bench tests finally established that each gallon of residue required treatment with 25 milliliters of Thio-Red in 1 gallon of water, with 50 pounds of fly ash needed to bind the mixture.

Method Development

Further testing involved scaled-up trials of this treatment. These trial runs, each using several gallons of reclaimer residue, were made to confirm the correct proportions, and to solve problems on how to conduct the mixing and safely deal with the hot solution. Several procedural lessons were learned from the scaled-up tests:

- 1) Some plastic buckets melted readily when filled with hot solution, so we chose to use steel buckets.
- 2) When mixing the fly ash and treated solution in a cement mixer, the solution should be added to the mixer first; otherwise the mixing is inefficient and incomplete.
- 3) To eliminate the need to heat the reclaimer drain line for residue transfer more than once, it was necessary to empty the entire reclaimer contents into a larger container while the residue was hot, and then to treat the entire 2,000 gallons of residue with water and Thio-Red while it was still warm.

- 4) We performed one trial using two mixers. The contents of one mixer set up while the workers were attempting to resolve a problem in the other mixer. We decided to use just one mixer to allow time to solve any other such problems.
- 5) It was necessary to use a raised platform to allow the cement mixer to completely empty into the receiving container.
- 6) Since the workers might be exposed to the residue directly, we detoxified the chromium before manual handling. This allowed us to reduce the level of personal protection required to that appropriate for mild, non-toxic materials.
- 7) We collected all solid waste, contaminated rags, and wash water in barrels. This was encapsulated in the last batch at the close of the operation.
- 8) The work was found to be strenuous enough that it could cause heat stress if performed on warm days; severe sunburn was also a risk. To avoid these problems, we decided to perform the work in the early morning hours or on cool days.

Based on the results of TCLP testing on the fly ash mixture, the Texas Natural Resources Conservation Commission (TNRCC) gave tentative approval for the proposed solidification procedures.

Implementation

The reclaimer residue was viscous enough that it would not flow at ordinary temperatures, but it could not be treated within the reclaimer still due to the limited capacity of the tank. Removal of the residue from the system would legally constitute generation of a hazardous waste. We needed a way to remove the hazard from the waste before we removed the waste from the system.

An empty 10,000 gallon capacity storage tank (Figure 3) which had been used to store the MEA used in the system was filled with 2,000 gallons of water and 50 liters of Thio-Red. Pressurized nitrogen (2-3 psig) was used to drive the 300°F residue out a bottom drain valve on the reclaimer still into a pipe directly into the prepared MEA storage tank. This action also served to improve safety by minimizing the need to handle the hot residue. Both an air stirrer and a circulating pump were used to stir the contents in the MEA tank to ensure thorough mixing.

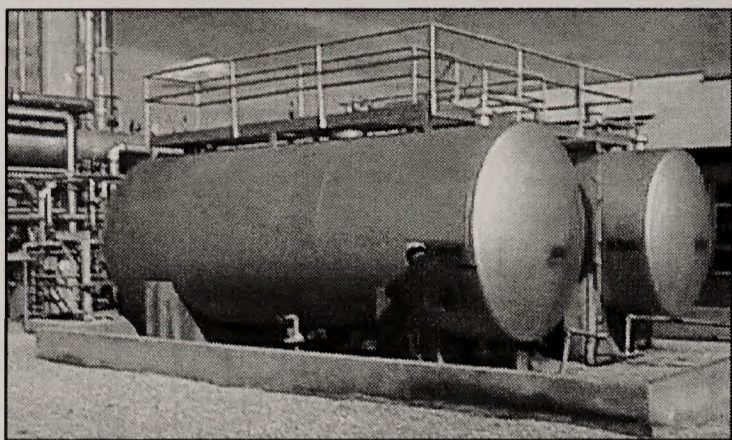


Figure 3: Monoethanolamine (MEA) storage tank

fork lift operations, and worker movement. A long garden hose was attached to a nearby source of flowing water for daily cleanup operations.

The workers actually involved in the mixing wore safety shoes, safety goggles or safety glasses, protective headgear, and heavy cotton clothing. Mixing was performed on intermittent days between 6:00 a.m. and 1:00 p.m. with rest periods. Cleanup at the end of mixing days typically required 1 to 1-1/2 hours.

The cement mixer used could mix three 80-pound bags of fly ash with 10 gallons of treated waste in a single batch.

Prefabricated wooden forms measuring approximately 11"x 42"x 35" outside dimensions were built to contain the fly ash mixture while it set into blocks. The forms were lined with plastic for easy removal of the cast block. To provide additional strength to the cement blocks, wire

The area between the reclaimer still and the MEA tank (Figure 4) provided sufficient space to perform the work while minimizing the distance materials would have to be moved manually. The work platform was erected adjacent to the MEA tank, and a cement mixer was placed on the work platform. Tarps were placed on the ground around the mixer and beneath the tap on the bottom of the MEA tank to catch spills. The area accommodated the treated residue buckets, the empty forms, the waste barrels, the fly ash pallet, and worker movement.



Figure 4: Work area between the reclaimer and the MEA tank, after cleanup.

mesh was placed within the forms before they were filled. The fly ash and treated waste were mixed together for 3-6 minutes before pouring the mixture into the forms. (Figure 5).

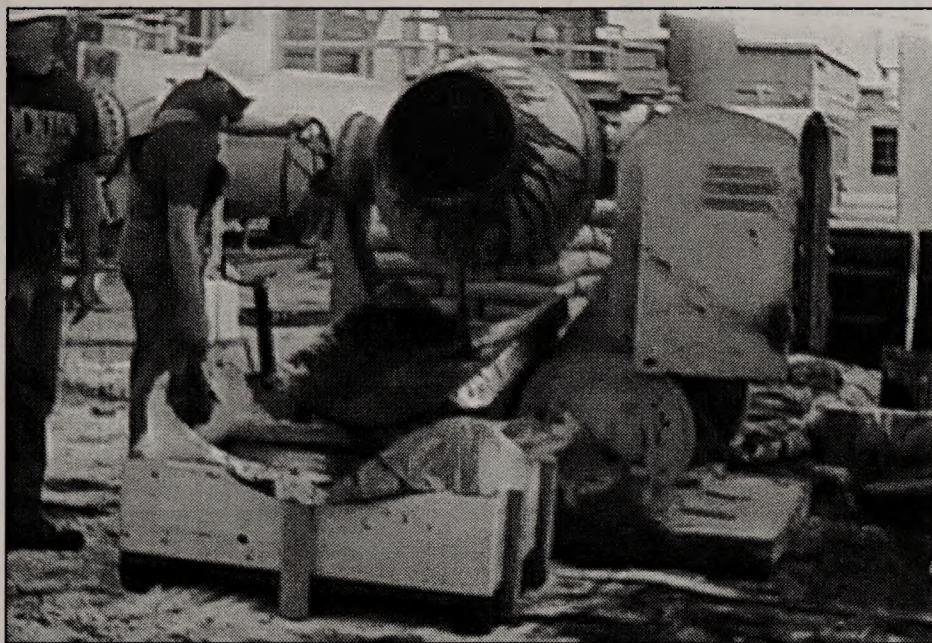


Figure 5: Workers pouring the treated waste into a form.

pour the blocks were removed from the forms and the forms were prepared for the next day of mixing. Weather forced cancellation of several scheduled days of mixing. During the entire production run, 121 cement blocks were produced by two workers in 11 days spent mixing and pouring.

A sample of the mixture was collected from each mixer load as the contents were poured into the form. Each day's samples were compiled as a composite sample of that day's work. The composite samples were then submitted to an independent laboratory (4) for TCLP analysis to confirm the effectiveness of each procedure. Table 1 summarizes the TCLP analyses.

Close-Out Actions

The final cleanup operation took 2 days, using both heavy equipment and manual labor. Contaminated rags and gravel, and some top soil that may have been contaminated, were treated with fly ash and water. The cement mixer retained a semi-hardened layer of treated waste and dried fly ash, which was removed using water under pressure and scraping. The wooden platform was disassembled. The mixer and other metal tools were cleaned and the washings were retained for future disposal. No known contamination was left on the operation site (Figure 4).

The processed blocks were moved to a designated solid waste management area on government property (Figure 6), as approved by the TNRCC. The trench reserved for final disposal of the blocks was sized to hold stacks of blocks four blocks high, three stacks to a rank, and ten ranks

Table 1. TCLP Analyses of Composite Samples

Date	Arsenic	Barium	Cadmium	Chromium	Lead	Selenium	Silver	Mercury
8 Aug 97 (AM)	ND	8.44	ND	0.68	ND	ND	ND	ND
8 Aug 97 (PM)	ND	8.6	ND	0.745	ND	ND	ND	ND
15 Aug 97	ND	10.3	ND	0.785	ND	ND	ND	ND
22 Aug 97	ND	10.2	ND	0.84	ND	ND	ND	ND
29 Aug 97	ND	2.64	ND	1.07	ND	ND	ND	ND
5 Sep 97	ND	7.93	ND	0.89	ND	ND	ND	ND
19 Sep 97	ND	3.28	ND	0.88	ND	ND	ND	ND
22 Sep 97	ND	8.22	ND	0.81	ND	ND	ND	ND
26 Sep 97	ND	3.98	ND	0.935	ND	0.255	ND	ND
29 Sep 97	ND	3.26	ND	0.93	ND	ND	ND	ND
3 Oct 97	ND	8.98	ND	1.02	ND	ND	ND	ND
16 Oct 97	ND	8.18	ND	0.765	ND	ND	ND	ND

ND = None Detected above estimated quantitation limit. All values in mg/L. Lead determined by EPA method 7470; all other metals determined by EPA method 6010.



Figure 6: Solid waste management area

deep. The trench was lined using a continuous layer of plastic, with excess width of plastic folded up over the sides of the stacked blocks. The empty spaces between the stacks were filled with used desiccant which was scheduled for disposal as part of the plant shutdown. The desiccant is expected to absorb any liquid that may leach out of the blocks over time. The top layer of blocks was covered with a thin layer of desiccant and another continuous layer of plastic. The stacks, including the desiccant packing and the plastic cover, were topped with a thin layer of dirt mixed with the remaining fly ash. A 4-inch layer of concrete was poured as a cap over the total interment. The concrete will be covered with native soil, and native vegetation will be planted to restore the surface to its original condition.

Conclusion

An economical method was developed to safely convert chromium in an amine/glycol solution into a material that is environmentally compliant with EPA and the RCRA. The estimated final cost of this project, including labor and materials, was less than \$30,000, resulting in a savings to the government of more than \$250,000 when compared to the cost of disposal under contract.

References

- (1) Sibrell, P.L., S.R.M. Burton, and D.E. Cornelius, "Analysis of Chromium in Amine/Glycol Solutions," U.S. Department of the Interior, Bureau of Land Management, Technical Note 400, June 1997
- (2) CAS #128587-22-3, obtained from ETUS, Inc., 1511 Kastner Place, Sanford, FL 32771
- (3) ENRECO Laboratories, 6661-A Canyon Drive, Amarillo, TX 79110 ph. 806-353-4425
- (4) Ana-Lab Corp., 4515 S. Georgia, Amarillo, TX 79110 ph. 806-355-3556

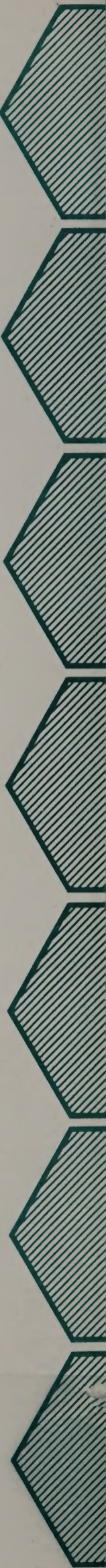
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